

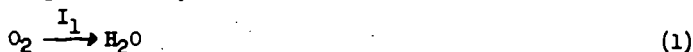
THE ROLE OF HYDROGEN PEROXIDE IN OXYGEN REDUCTION
AT Pt, Rh AND Au ELECTRODES

M. A. Genshaw, A. Damjanovic and J. O'M. Bockris

The Electrochemistry Laboratory
The University of Pennsylvania
Philadelphia, Pa. 19104

For oxygen reduction at electrodes in acid solutions, some workers have reported^{1,2} that oxygen reduces only to water, others that hydrogen peroxide is either an intermediate in the reduction to water or a product in the reduction.³⁻⁸ A similar situation exists for alkaline solution where hydrogen peroxide appears to be a reaction intermediate which reduces further.

Little or no attention was paid to the possibility that parallel reactions may be present. In one reaction, oxygen could be reduced to water without hydrogen peroxide as a stable intermediate. In the other, hydrogen peroxide could form as a reaction intermediate which then reduces at least partially to water. These parallel reactions may be represented by



Hydrogen peroxide, which is an intermediate in path (2), is partially reduced to water and partially diffuses away from the electrode. I_1 , I_2 and I_3 are the corresponding currents, and I_4 represents the rate by which H_2O_2 diffuses away.

Recently, it was demonstrated that it is possible to analyze these parallel reaction paths, and to determine whether hydrogen peroxide is a reaction intermediate in a single reaction path, or a product in a reaction path parallel to that in which oxygen is reduced to water without hydrogen peroxide intermediate.⁹ For this analysis, a rotating disk electrode with a concentric ring is used.

In this communication, the application of the rotating disk electrode with the concentric ring in the study of oxygen reduction at Pt, Rh and Au disk electrodes in acid and alkaline solutions is described, and some data are presented and discussed.

If hydrogen peroxide is formed at the test, the disk electrode, kept at a required potential, it may diffuse away from the disk to the ring electrode. The potential of the ring electrode is kept at 1.4 V* so that all hydrogen peroxide which diffuses to the ring electrode is oxidized and detected. For the current at the disk electrode at a given potential, I_d , and the current at the ring electrode, I_r , the following relationship holds

$$\frac{I_d}{I_r} = \frac{x+1}{N} + \frac{x+2}{N} \cdot \frac{\nu^{1/6} k_3}{D^{2/3} \omega^{1/2}} \quad (3)$$

Here, N is a geometrical factor which depends on the dimensions of the disk and

*All potentials are with respect to the hydrogen electrode in the same solution.

ring electrodes, D is the diffusion coefficient for the reaction intermediates, ν is kinematic viscosity, k_3 is the rate constant for the reduction of H_2O_2 intermediate at the disk electrode and ω is the rate of disk rotation. In this equation, x is defined as

$$x = I_1/I_2 \quad (4)$$

with I_1 being the partial current due to the reduction of oxygen to water in the path without hydrogen peroxide intermediate, and I_2 the partial current due to the reduction to hydrogen peroxide.

From the plots of I_d/I_r against $\omega^{-1/2}$ the intercept with the I_d/I_r axis,

$$\text{Intercept} = (x + 1)/N, \quad (5)$$

can be read. With N known, x can be calculated and hence the ratio I_1/I_2 obtained.

Pt, Rh and Au disk electrodes are examined in acid (0.1 N H_2SO_4) and alkaline (0.1 N KOH) solutions saturated at room temperature by O_2 under 1 atm. pressure. Currents at the disk and ring electrodes have been measured as functions of the disk potential and for various rates of disk rotation.

For Pt electrode in acid solution the plots of I_d/I_r against $\omega^{-1/2}$ consists of a series of lines parallel to the $\omega^{-1/2}$ axis (Fig. 1). Each line corresponds to a given potential of the disk electrode and has an intercept with I_d/I_r axis greater than $1/N$. Hence, oxygen reduction proceeds along two parallel reaction paths. Hydrogen peroxide is produced in a path parallel to the reaction path which does not involve H_2O_2 as an intermediate. At potentials anodic to, say, 0.60 V, the intercepts are all greater than 20, and $x \gg 7.6$ ($N = 0.38$). Hence, the major reaction is that in which O_2 is reduced to H_2O without H_2O_2 intermediate (90% or more of the total current). Since the slopes of the lines are zero, k_3 in equation (3) is small. It implies that H_2O_2 formed in the parallel reaction path is not reduced further to water with any rate comparable to that by which it is produced.

The solution in which the above experimental data are obtained was prepared from "Baker Analyzed Reagent" H_2SO_4 and conductivity water. However, if this solution was further purified electrochemically, no hydrogen peroxide is detected to form at potentials anodic to 0.150 V. Such a different behavior of the electrode in "pure" and "insufficiently" purified solutions is believed to be due to the adsorption at the electrode surface of residual, mostly organic, impurities from the solution.

At Pt electrode in alkaline solution, I_d/I_r plots reveal that oxygen reduction proceeds with comparable rates along two reaction paths (Fig. 2). In one of these paths, hydrogen peroxide is an intermediate which partially reduces further. In contrast to Pt electrode in acid solution, Pt electrode in alkaline solution appeared to be not affected by the presence of residual impurities in the solution.

Similar experiments with Rh in acid solution showed that the behavior of the electrode is also affected by purification of the solution. In "insufficiently" purified solutions, H_2O_2 is formed in a path parallel to that in which O_2 is reduced to water without hydrogen peroxide as an intermediate. The major reaction is the reduction to H_2O without hydrogen peroxide intermediate. In contrast to a Pt electrode, at potentials cathodic to 0.60 V hydrogen peroxide formed at Rh electrode reduces, at least partially, further to water. In "pure" acid solutions oxygen reduction at Rh electrode proceeds along a single reaction path which does not involve hydrogen peroxide intermediate. In alkaline solution, the major reaction path is that in which O_2 is reduced to hydrogen peroxide. Hydrogen peroxide reduces further to water.

For a gold electrode in acid solution, the current-potential relationship for oxygen reduction has a characteristic "S" shape. This is illustrated in Figure 3. Two linear regions in V -log i plots are evident, each with a slope close to $-2RT/F$. Similar results have previously been reported.⁷ Reaction path for oxygen reduction in these two regions can now be examined by the disk electrode with a concentric ring.

The plots of I_d/I_r against $\omega^{-1/2}$ are shown in Figures 4 and 5. In the potential range 0.55 - 0.65 V, the I_d/I_r lines have negative slopes at smaller values of $\omega^{-1/2}$. The lines are essentially parallel to the $\omega^{-1/2}$ axis from 0.50 to 0.25 V but show positive slopes at 0.20 V and more cathodic potentials. The intercepts of the lines with the I_d/I_r axis in the potential range 0.00 to 0.35 V are clustered between 2.7 and 3. At higher potentials, the intercepts increase with increasing potential. In contrast to Pt and Rh, oxygen reduction at Au electrodes is not affected by the presence of residual impurities in solution.

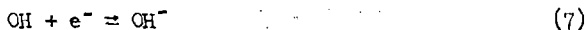
From the intercept given by (5), and with N equal to 0.39, it appears that at and below 0.30 V x is small. With $x \approx 0$, oxygen reduction at Au in acid solution proceeds along a single reaction path with hydrogen peroxide as an intermediate. At and below 0.20 V, hydrogen peroxide intermediate reduces further to water with a rate which increases with decreasing electrode potential. In the potential region 0.35 - 0.55 V, $x \neq 0$ and hence oxygen reduction proceeds with nearly equal rates along two parallel reaction paths. At still higher electrode potentials, the major reaction is the reduction of oxygen to water without hydrogen peroxide intermediate. Hydrogen peroxide which at these high potentials forms in a parallel path does not reduce to water with any significant rate. A representation of this discussion is shown also in Figure 3. Just at the potential at which there is the change from one Tafel region in the V -log i curve to the other, the change in the importance of the reaction paths occurs. Thus, at potentials anodic to 0.60 V, oxygen is reduced mainly to water while at potentials cathodic to 0.5 V, the main path is that in which oxygen is reduced to hydrogen peroxide.

The characteristic change in the V -log i curve at a current of about $5 \cdot 10^{-6} A$ resembles the attainment of a limiting current for the reaction which predominates in the low current density region, until another reaction, which predominates in the high current density region, takes over. It is difficult to see any reason for this change in the reaction other than the surface heterogeneities. If heterogeneity of the electrode surface is assumed, about 1% of some active "sites" will be enough to sustain the major reaction in the region of low currents. Negative slopes of I_d/I_r lines in Figure 5, suggest also that this major reaction, which is reduction of oxygen to water, occurs at some active "sites." These slopes are observed in the current region in which the reduction to water becomes apparently diffusion controlled. With increasing rate of disk rotation, diffusion of oxygen to these "sites" increases and so does the current for the reduction of oxygen to water. Consequently, the disk current increases while the ring current remains unchanged, and, for the same electrode potential, I_d/I_r decreases with increasing $\omega^{-1/2}$.

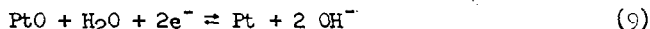
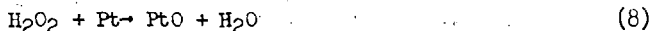
In alkaline solution at gold electrode it appears that oxygen reduction proceeds along a single reaction path with hydrogen peroxide as an intermediate which reduces further to water.

From the slopes of the lines of I_d/I_r against $\omega^{-1/2}$, k_3 in equation (3) can be calculated for a given potential. In Figure 6, log k_3 is plotted against potential for the reduction at Pt electrodes in alkaline solution. If a straight line were drawn through the points, the slope would be about 0.6 V. This unusually high slope for the change of the log rate with potential probably indicates that the reduction of hydrogen peroxide is controlled by a chemical rather than a charge transfer step. Accordingly, two possible mechanisms for the reduction of hydrogen

peroxide at Pt in alkaline solution may be suggested:



or



These mechanisms are indistinguishable by usual electrochemical means. Similar situation exist for Rh and Au electrodes in alkaline solution.

The above examples clearly demonstrate the complexity of oxygen reduction at electrodes. More often than not, parallel reaction paths are present, particularly at lower potentials and insufficiently pure solutions. If hydrogen peroxide formed in a parallel reaction or as a reaction intermediate in a single reaction path, it may reduce further with the rate lower than that by which it is formed. The same examples also illustrate the suitability of the rotating disk electrode with the concentric ring in the study of parallel reaction paths.

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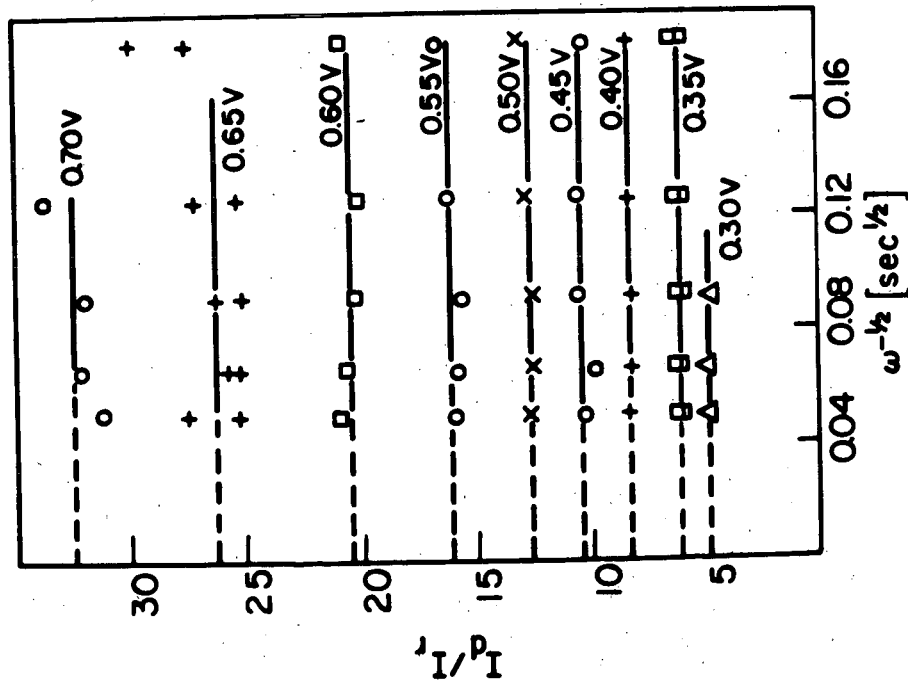


FIG.1 I_d/I_r against rate of disk rotation.
Pt in 0.1N H₂SO₄.

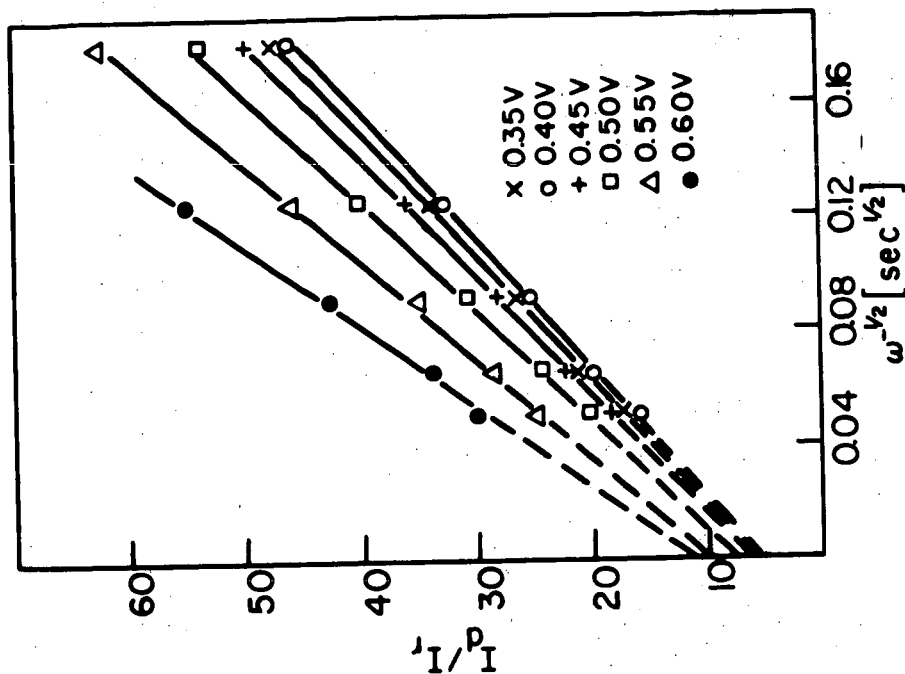


FIG.2 I_d/I_r against rate of disk rotation.
Pt in 0.1N KOH.

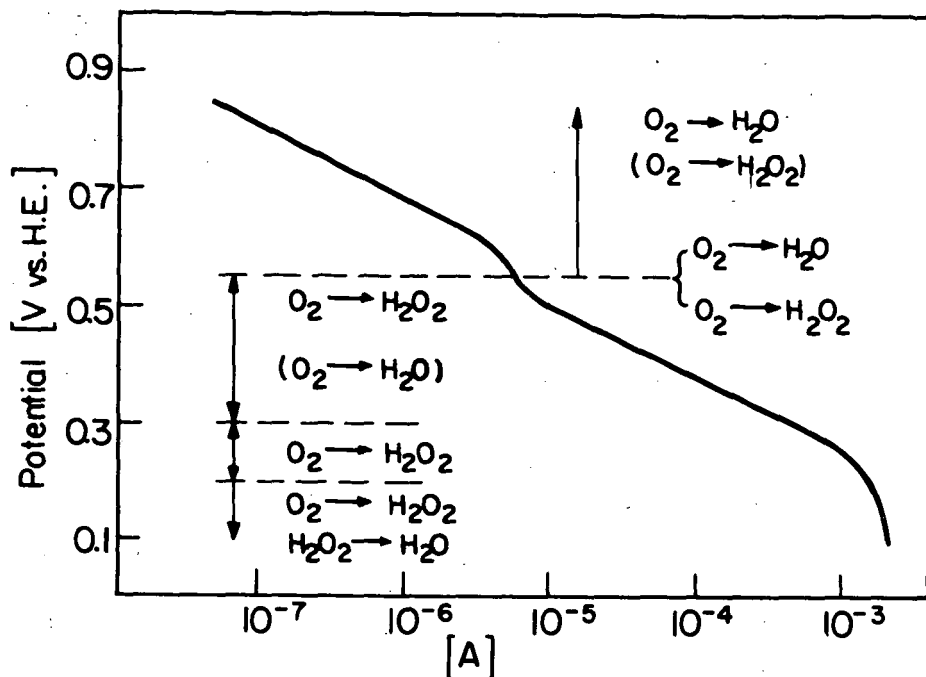


FIG.3 Disk current. Au in 0.1N H_2SO_4 . Minor reaction given in brackets.

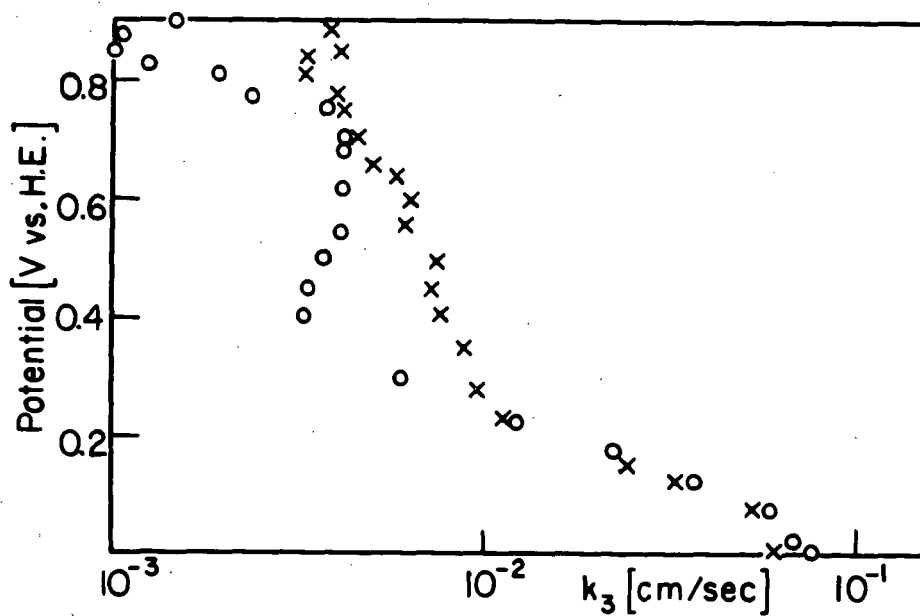


FIG.6 k_3 vs. potential plot. Pt electrode in alkaline solution. Two measurements.

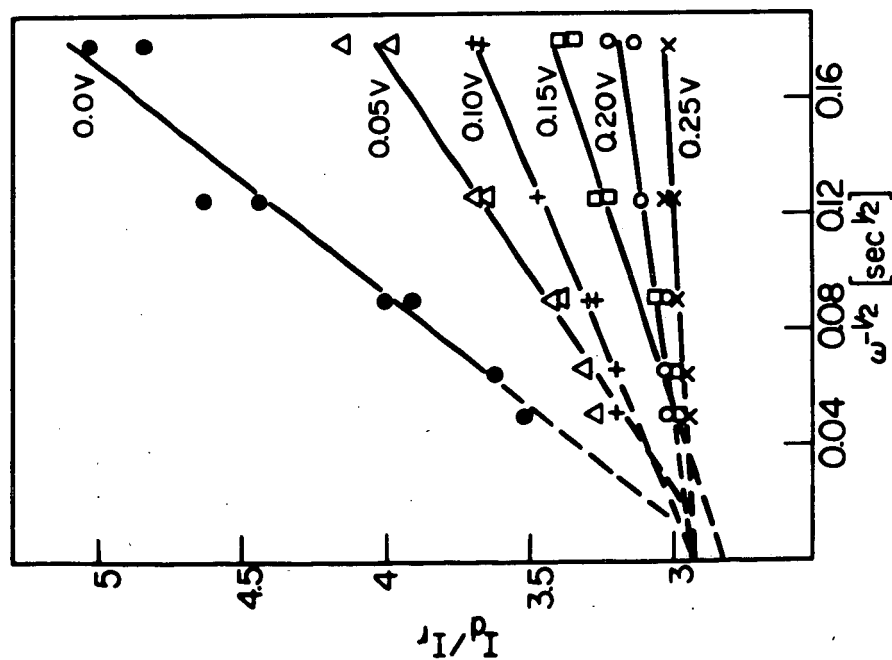


FIG.4 I_d/I_r , against rate of disk rotation.
Au in 0.1N H₂SO₄.

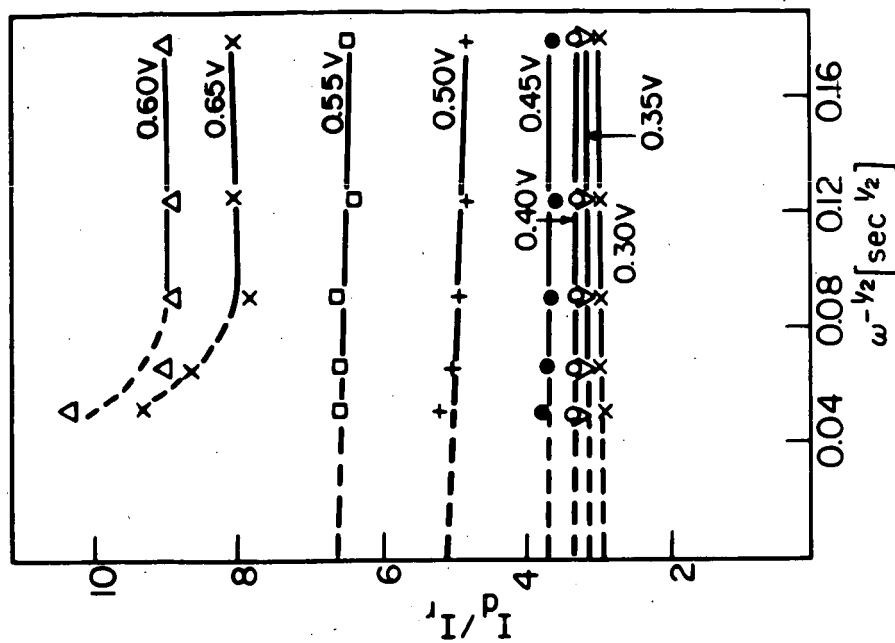


FIG.5 I_d/I_r , against rate of disk rotation.
Au in 0.1N H₂SO₄.